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Effect of key operating parameters on the non-catalytic wet oxidation of olive mill wastewaters

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Abstract The non-catalytic wet air oxidation (WAO) of olive mill wastewaters was investigated. The effect of operating conditions, such as initial organic loading (1000 and 4500 mg/L COD), reaction temperature (140 and 180°C), treatment time (1 and 4 h), initial pH (4.8 and 7) and the use of 500 mg/L H_2O_2 as an additional oxidant, on treatment efficiency was assessed implementing a factorial experimental design. Of the five parameters tested, the first two had a considerable effect on COD removal, while treatment time was of no significance implying that all oxidation reactions occur during the first hour of treatment. Although the level of mineralization was generally moderate, this was accompanied by nearly complete total phenols and color removal. The analysis was repeated at more intense conditions, i.e. initial COD up to 8000 mg/L and reaction temperature up to 200°C; at this level, none of the studied effects were important. However, at optimal experimental conditions (i.e. 180°C, 1 h treatment and initial COD of 8100 mg/L) WAO yielded 34, 94 and 74% removal of COD, total phenols and color respectively. Moreover, ecotoxicity to *V. fischeri* was slightly reduced after 2 h of treatment at the above conditions.
Keywords Factorial design methodology; olive mill wastewater; treatment; toxicity; wet air oxidation

INTRODUCTION

Olive oil extraction is an economically important activity for many regions of the Mediterranean Sea area. This process results in large quantities of bio-recalcitrant effluents that come from the vegetation water and the soft tissues of the olive fruits mixed with the water used in the different stages of oil production. All these wastewaters, together with the industry washing waters, make up the olive mill wastewater (OMW), whose COD content may reach values up to 100-150 g/L and its phenolic content (mainly responsible for the recalcitrant and antibacterial behavior) up to 24 g/L (Niaounakis and Halvadakis, 2006).

Dumping OMW in evaporation ponds is the most common management practice in Greece (and elsewhere in the Mediterranean). In some cases, lagooning is coupled with lime coagulation to remove suspended solids. Unfortunately, this practice suffers from serious drawbacks such as high cost, low efficiency and sludge-disposal problems. Interestingly and depending on the climatic conditions, OMW may not evaporate by the end of the summer, thus making the pond unavailable to accept the following year's load. Moreover, fermentation processes may occur in weathered

OMW, thus resulting in the formation of methane and other gases; OMW can become extremely malodorous especially between late spring and summer. In this view, increasing concern has been expressed about the effective treatment of OMW.

Research efforts have been directed towards the development of efficient treatment technologies, including several physical, chemical and biological processes, as well as various combinations of them (Mantzavinos and Kalogerakis, 2005). Advanced oxidation processes (AOPs) have been employed as alternative pretreatment methods aiming at reducing organic load and bio-recalcitrance of these wastewaters. Wet air oxidation (WAO) belongs to the family of AOPs and is a thermochemical process whereby hydroxyl radicals and other active oxygen species are formed at elevated temperatures (i.e. 200-320°C) and pressures (i.e. 2-20 MPa) (Levec and Pintar, 2007). The process is known to have great potential for the treatment of wastewaters with moderate to high organic content (i.e. 10-100 g/L COD) converting dissolved organic pollutants into highly oxidized intermediates and eventually to carbon dioxide and water. Several studies which are summarized in recent review articles (Bhargava et al., 2006; Levec and Pintar, 2007) have reported the use of WAO to treat various types of effluents.

Regarding OMW, Gomes et al. (2007) found that catalytic WAO using Pt/C as a catalyst at 200^{o}C and an oxygen partial pressure of 0.69 MPa resulted in mineralization and complete color removal from an effluent with an initial COD of 6.05 g/L. Copper- and iron-pillared clay catalysts showed comparable performances during the wet hydrogen peroxide oxidation of OMW at 70^{o}C (Caudo et al., 2007). Specifically, after 4 h of treatment (initial total organic carbon (TOC) of 14 g/L and total phenols (TPh) of 390 mg/L), TOC and TPh removal was about 20 and 45% respectively. In other studies (Rivas et al., 2001), OMW at 14.65 g/L initial COD was also treated by WAO and it was found that the addition of hydrogen peroxide enhanced significantly treatment efficiency and so did the presence of catalysts such as Pt/Al_2O_3 and CuO/C. Catalytic (platinum and ruthenium supported on titania or zirconia) WAO experiments at 190^{o}C and 7 MPa total pressure confirmed the effective elimination of TOC and TPh in diluted OMW (Minh et al., 2008).

The aim of this work was to study the non-catalytic wet air oxidation of OMW regarding the effects of various operating conditions such as initial organic loading, reaction temperature, initial pH, treatment time and the addition of hydrogen peroxide on the conversion of COD, TPh and color.

MATERIALS AND METHODS

OMW

The OMW was provided by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. Following filtration to remove 99% of total solids, the effluent contained 40 and 3.5 g/L of dissolved COD and TPh respectively. Prior to reaction, the effluent was diluted with distilled water to achieve initial concentrations between 1 and 8 g/L COD. This level of dilution (i.e. between 5 and 40 times) is consistent with previous studies on catalytic WAO reporting OMW dilution factors between 2 and 70 (Rivas et al., 2001; Caudo et al., 2007; Gomes et al., 2007; Minh et al., 2008).

WAO experiments

A high pressure reactor (Parr Instruments, USA) made of alloy C-276 and capable of operating at pressures up to 21 MPa and temperatures up to 350°C was used. In a typical semibatch run, 0.35 L of diluted OMW was batch loaded into the reactor which was then heated up to the operating temperature under continuous nitrogen flow. This procedure was used to minimize unwanted conversion during the heating-up period. As soon as the desired temperature was reached, oxygen was continuously sparged into the reactor to start the reaction and the oxygen partial pressure was maintained at 2.5 MPa, where oxidation is not limited by the amount of oxygen dissolved (Katsoni et al., 2008). The reactor contents were stirred at 800 rpm ensuring good mass transfer from the gas to the liquid phase.

When hydrogen peroxide was used as an extra oxidant, the appropriate amount of a 35% w/w solution was added to achieve a 500 mg/L H_2O_2 initial concentration. Liquid samples of approximately 10 mL were periodically withdrawn from the reactor through a tube located inside the reactor vessel and analyzed as follows.

Analytical measurements

COD was determined by the dichromate method according to Standard Methods (1998). The total phenolic (TPh) content was determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin-Ciocalteau reagent according to the procedures described in detail elsewhere (Singleton et al., 1999). Gallic acid monohydrate was used as standard to quantify the concentration of phenols in OMW. Changes in sample absorbance at 550 nm were monitored to assess the extent of decolorization that had occurred during treatment.

H_2O_2 concentration in the OMW solution was monitored using Merck peroxide test strips (0-25 mg H_2O_2/L and 0-100 mg H_2O_2/L). The effluent pH was checked by a Toledo 225 pH meter during WAO.

The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of OMW samples prior to and after treatment. The inhibition of bioluminescense of *V. fischeri* was measured using a LUMIStox analyzer (Dr. Lange, Germany). Toxicity is expressed as EC_{50}, which is the effective concentration of a toxicant causing 50% reduction of light output after 15 min at 15^{o}C.

Statistical treatment

In this work, a statistical approach was chosen based on a factorial experimental design to infer about the effects of the variables on treatment performance. Five independent variables (X_1 to X_5) that typically affect WAO efficiency were taken into account, namely initial COD concentration, reaction temperature, initial solution pH, H_2O_2 concentration and treatment time. Each one of them received a high and a low value as seen in Table 1. WAO efficiency was evaluated in terms of mass of COD oxidized (response factor Y_1) and mass of TPh removed (response factor Y_2).

The experimental design followed in this work was a full 2^5 experimental set, which required 32 experiments. The design matrix of the experiments and their statistical analysis were made by means of the software package Minitab 14 (Minitab Inc., USA). Analysis of the response factors Y_1 and Y_2 involves the estimation of the average effect, the main effects of each individual variable, as well as their two and higher order interaction effects (Daniel, 1976; Box et al., 1978).

A key element in the factorial design statistical procedure is the determination of the significance of the estimated effects. Lenth's method was used for the assessment of the significance of the main and interaction effects in un-replicated factorial designs (Lenth, 1989). Lenth's method assumes that all independent effects have the same variance. According to this method, the pseudo-standard error (PSE) is estimated and it is then multiplied by a factor to obtain a margin of error (ME) for the effects. An important concern is that several inferences are being made simultaneously. With a large number of effects, it is expected that one or two estimates of inactive effects will exceed the ME leading to false conclusions. To account for this possibility, a simultaneous margin of error (SME) is also defined for a 95% confidence interval.

All estimated effects greater than the ME, in absolute values, are deemed significant. On the other hand, all other effects whose values are lower than the ME can be attributed to random statistical error. Moreover, an effect that exceeds the ME but not the SME should be viewed with some caution, as it may be an artifact of testing several effects (Lenth, 2006).

RESULTS AND DISCUSSION

Determination of statistically significant parameters

The results of the 2^5 factorial design in terms of the response factors Y_1 and Y_2, as well as the extent of COD, TPh and color removal are given in Table 1, while the calculated values of the average, main and interaction effects are given in Table 2.

A useful pictorial presentation of the estimated effects and their statistical importance can be accomplished using the Pareto chart which displays the absolute values of the effects, as well as the ME and SME decision lines. The Pareto chart of the effects for COD oxidation is shown in Figure 1a. Undoubtedly, the most important effect is the influent COD, revealing a positive effect on treatment efficiency. This means that an increase in its level brings about an increase in the amount of COD oxidized. For instance, comparison of Runs 15 and 2 or 7 and 30 in Table 1 shows that a 4.5-fold increase in influent COD yields a 5-fold increase in the amount of COD oxidized with all other variables being identical. Moreover, reaction temperature yields a positive effect, while pH affects negatively COD removal indicating that a decrease in its level brings about an increase in the amount of COD oxidized. Based on the variables and interactions which are statistically significant, a model describing the experimental response for COD removal was constructed as follows:

$$Y_1 = 580.4 + 365.2X_1 + 150.1X_2 - 138.2X_3 + 126.8X_1X_2 - 121.2X_1X_3 \qquad (1)$$

where X_i are the transformed forms of the independent variables based on the original values Z_i according to:

$$X_i = \frac{Z_i - \frac{Z_{high} + Z_{low}}{2}}{\frac{Z_{high} - Z_{low}}{2}}$$

The coefficients appearing in eqn (1) are half the calculated effects of Table 2, since a change of X=-1 to X=1 is a change of two units along the X axis.

The validation of the above model was based on the calculation of the residuals which are the observed minus the predicted values. The normal plot of residuals revealed that all data points lay close to a straight line and within the 95% confidence interval lines (plot not shown for brevity). This indicates that there was a good agreement between the experimental values and the mathematical model developed, while the observed differences could be readily explained as random noise.

Figure 1b displays the Pareto chart for TPh removal. The results are consistent with those obtained for COD removal pointing out that influent COD is the most significant variable affecting positively TPh removal. Besides, reaction temperature is significant for treatment performance both as an individual effect and through its interaction with hydrogen peroxide. On the other hand, pH results in a negative effect on performance through its interaction with temperature or initial COD. Based on the variables and interactions which are statistically significant, a model describing the experimental response for TPh removal was constructed as follows:

$$Y_2 = 201.9 + 133.7X_1 + 22.9X_2 - 21.2X_2X_3 + 23.2X_2X_4 - 19.3X_1X_2X_3 \qquad (2)$$

Again, the residuals for TPh removal were calculated and the normal plot of residuals was constructed (data not shown for brevity). All points lay close to a straight line confirming the conjecture that effects other than those considered in the model could be readily explained as random noise.

It is interesting to note that treatment time does not affect significantly WAO performance in terms of TPh and COD removal. This means that at the selected low and high values of treatment time (i.e. 1 and 4 h respectively), removal remains practically unchanged, implying that most of the oxidation mainly takes place during the first hour of the process.

Moreover, the addition of H_2O_2 has no effect on COD removal and only marginal effect on TPh removal through its interaction with temperature. Generally, the addition of hydrogen peroxide is expected to enhance process efficiency since its thermal decomposition yields two hydroxyl radicals per molecule of H_2O_2 decomposed. The last column of Table 1 shows that, in nearly all cases, the residual oxidant concentration is negligible, thus indicating its rapid consumption within the early stages of reaction. This, in turn, implies that 500 mg/L of H_2O_2 is either too low to promote substantially oxidation reactions or the oxidant is inefficiently utilized and wasted through unwanted reactions. For instance, the instantaneous injection of hydrogen peroxide may result in excessive localized oxidant concentrations that scavenge a fraction of hydroxyl radicals and other reactive species (Rivas et al., 1998), while the stepwise, continuous addition may reduce the extent of scavenging reactions and consequently enhance degradation (Caudo et al., 2007).

Treatment at more intense conditions

It was then decided to proceed with a new factorial design to further investigate the effect of three variables, namely influent COD, temperature and treatment time. The experimental design followed in this case was a full 2^3 experimental set. The values chosen for the independent variables, the obtained results in terms of mg/L of COD and TPh oxidized, as well as the extent of decolorization, COD and TPh removal are presented in Table 3.

Regarding the other operating parameters, initial solution pH was about 4.5 and it was left unchanged as acidic conditions were found to promote degradation. Moreover, during WAO the majority of contaminants remain in the aqueous phase forming inorganic salts and acids (Kolaczkowski et al., 1999). The production of acids results in a decrease in the pH of the aqueous phase that was evident in the present study. In particular, a reduction of about 1 and 0.5 pH unit was recorded at high (i.e. 4 h) and low (i.e. 1 h) treatment times respectively. No H_2O_2 was added as this had little effect on performance.

Estimation of the average effect, the main effects of the three variables and their interaction appears in Table 4. An estimate of the standard error was obtained by performing triplicates at the center point of the factorial design, i.e. the variables receive mean values between their high and low levels. The standard error (SE) is also shown in Table 4. To identify important effects when replicated experiments are carried out, the corresponding p-values are computed. If the p-value is $\geq$0.05 that effect is not statistically significant at the $\geq$95% confidence level. Hence, it is evident from Table 4 that none of the independent variables were significant for treatment efficiency, since the p-values of the effects or their interactions are always greater than 0.05.

This is demonstrated clearly in Figure 2 where changes in COD and TPh are plotted as a function of treatment time during WAO at initial COD of 4500 or 8100 mg/L and at 180 or 200°C. It is worth noticing that after 0.5-1 h of treatment, COD and TPh removal remains practically unchanged under all experimental conditions. Therefore, all oxidation reactions take place during the first hour of WAO treatment reaching a plateau above this point. It is well documented (Rivas et al., 1999; Azabou et al., 2007) that the WAO of organics occurs through two stages, an initial fast period in which conversion increases rapidly with time, followed by a slower second stage where conversion remains practically unchanged. This is due to the fact that organics cannot be further mineralized by WAO treatment. The larger molecules are decomposed to smaller refractory organic molecules which are hard to oxidize. This appearance of a plateau for COD removal due to recalcitrant organic compounds, like low molecular weight carboxylic acids which are not further oxidized even after prolonged times of non-catalytic wet air oxidation has been widely reported (Debellefontaine et al., 1995; Mantzavinos et al., 1996; Gomes et al., 2007).

Noticeably, there is no temperature dependence regarding treatment efficiency in the range 180-200°C. It has been reported that temperature increase influences WAO performance up to a value, above which further increases do not practically affect reaction rates (Bhargava et al., 2006).

Mineralization, decolorization and detoxification

In general and as seen in Tables 1 and 3 and Figure 2, phenols are easily oxidized under almost all experimental conditions. On the other hand, other compounds that were originally present in OMW or formed as secondary reaction by-products are more resistant to wet oxidation and this is consistent with the substantially lower COD conversion. Gomes et al. (2007) reported that the non-catalytic WAO of OMW (initial COD of 6.05 g/L) resulted in 53% mineralization after 2 h at 200°C which is comparable to the performance recorded in this work at similar conditions (e.g. Run 6

in Table 3). In other studies (Rivas et al., 2001), the non-catalytic WAO for 3 h at 14.65 g/L initial COD, 180°C, 7 MPa total pressure and pH_0=5.3 led to about 20% COD and 50% TPh removal; these conversions are lower than those recorded in this work (e.g. Figure 2 at 8100 mg/L COD and 180°C showing 45% COD and 95% TPh removal after 3 h) presumably due to the nearly twofold initial concentration.

Noticeably, increased TPh degradation is accompanied by a consistently high effluent decolorization; this is expected since the dark color of OMW is associated, to a great degree, with the presence of polyphenolic compounds (Gotsi et al., 2005; Chatzisymeon et al., 2008). On the assumption that TPh are represented by gallic acid (monohydrate), the stoichiometry of its reaction to carbon dioxide and water dictates that 100 mg of gallic acid would require 102 mg oxygen for the complete oxidation; therefore, the Y_2 column of Tables 1 and 3 practically corresponds to the concentration of COD oxidized due to the phenolic fraction of the effluent. In this view, the discrepancy between the Y_1 and Y_2 columns of Tables 1 and 3 is a measure of the oxidizability of effluent's fractions other than TPh. It is obvious that WAO is a non-selective process attacking simultaneously various organic fractions.

Toxicity measurements were done for OMW samples prior to and after treatment. In particular, the untreated effluent at an initial COD of 8100 mg/L was highly ecotoxic to *V. Fischeri* with an EC_{50} value of 4.3%. Following WAO, toxicity remained practically unchanged (i.e. EC_{50} was 3.6 and 3.5% after 0.5 and 1 h of treatment respectively), while a slight reduction was recorded after 2 h of oxidation with EC_{50} becoming 11%. It should be noted that the residual TPh in the effluent after 0.5, 1 and 2 h of treatment was 104, 48 and 41 mg/L respectively; this implies that persistent ecotoxicity is likely to be due to several organic compounds other than the polyphenolic fraction of OMW. Similar results were obtained at an initial COD of 4500 mg/L. Toxicity reduction was about the same yielding an EC_{50} value of 14% after 2 h of WAO. Minh et al. (2008) reported that the strong toxicity of untreated OMW (initial TOC of 4-5 g/L) to *V. Fischeri* was only partly removed after several (i.e. >20) hours of catalytic WAO at 190°C although the treated effluent contained no TPh; residual toxicity was attributed to the formation of refractory, toxic by-products.

CONCLUSIONS

Wastewater from the olive oil industry was treated by wet air oxidation with emphasis given on the effect of various operating conditions on treatment efficiency with regard to COD, TPh and color removal. In order to evaluate the importance of the various parameters involved in a coherent way, a factorial design methodology was followed.

Eventually, it was inferred that treatment efficiency, regarding COD and TPh removal, is mainly enhanced at increased influent COD values. This is an important consideration for the treatment of actual effluents at industrial scale since dilution should be kept to a minimum. WAO of OMW at 8100 mg/L influent COD and 180^{o}C for 1 h led to 34, 94 and 74% COD, TPh and color removal respectively.

The ecotoxicity of original, diluted OMW is high and it was only slightly reduced following oxidation; this is probably due to the presence of various toxic species that remain in the treated effluent at considerably high concentrations.

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Table 1. Design matrix of the 2^5 factorial experimental design, levels of independent variables (X_1 to X_5) and observed response factors (Y_1: mass of COD removed per liter; Y_2: mass of TPh removed per liter), as well as percent removal of COD, TPh and color. ND: not determined.

Run order	X_1 $[COD]_0$, mg/L	X_2 Temperature, °C	X_3 pH_0	X_4 $[H_2O_2]$, mg/L	X_5 Treatment time, h	Y_1 COD oxidized, mg/L	Y_2 TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal	Residual H_2O_2 after treatment, mg/L
1	4500	140	7	0	4	550	391	11	94	90	0
2	4500	180	7	0	1	770	246	17	88	77	0
3	4500	140	7	500	4	720	352	15	97	93	3
4	1000	180	7	500	1	288	83	31	99	100	3
5	1000	140	4.8	500	1	260	19	26	83	98	10
6	4500	140	4.8	0	1	370	258	11	68	ND	0
7	1000	180	4.8	500	4	396	105	39	100	100	0
8	1000	180	4.8	0	4	186	55	21	60	100	0
9	4500	180	4.8	0	1	1370	348	35	98	91	0
10	1000	140	4.8	0	4	156	55	18	83	93	0
11	1000	180	7	0	4	196	107	21	100	100	0
12	4500	140	4.8	0	4	970	319	29	84	ND	0
13	4500	140	7	0	1	410	349	8	84	59	0
14	1000	180	4.8	0	1	88	14	10	89	100	0
15	1000	180	7	0	1	140	96	15	98	100	0
16	1000	140	4.8	500	4	332	31	33	100	94	0.5
17	4500	140	7	500	1	430	316	9	87	81	10
18	1000	140	7	0	4	150	73	15	94	100	0
19	4500	140	4.8	500	4	1290	284	27	85	82	0
20	4500	180	4.8	500	1	1480	434	30	95	63	0
21	4500	180	7	0	4	1080	268	23	95	97	0
22	1000	140	7	500	1	218	44	21	98	100	50
23	1000	180	7	500	4	298	92	32	100	100	0
24	4500	140	4.8	500	1	610	220	13	66	3	0
25	1000	140	7	0	1	88	69	9	88	82	0
26	1000	180	4.8	500	1	316	97	31	99	99	1
27	4500	180	7	500	1	750	371	16	96	85	10
28	1000	140	4.8	0	1	124	41	14	61	ND	0
29	4500	180	4.8	0	4	1660	350	43	100	100	0
30	4500	180	4.8	500	4	1890	463	38	85	85	0
31	1000	140	7	500	4	208	30	20	91	100	1
32	4500	180	7	500	4	780	388	17	100	95	5

Table 2. Average and main effects of the independent variables and their two and higher order interactions of the 2^5 factorial design on the response factors Y_1 and Y_2.

Effect	Value of Effect	
	COD removal (Y_1)	TPh removal (Y_2)
Average Effect	580.4	201.9
Main Effects		
x_1	730.4	267.4
x_2	300.1	45.8
x_3	-276.4	7.2
x_4	122.4	13.9
x_5	196.9	18.2
Two-factor Interactions		
$x_1 x_2$	253.6	1.6
$x_1 x_3$	-242.4	-6.6
$x_1 x_4$	-26.1	23.4
$x_1 x_5$	146.9	15.9
$x_2 x_3$	-109.1	-42.4
$x_2 x_4$	-33.9	46.3
$x_2 x_5$	-36.4	-9.2
$x_3 x_4$	-83.9	-4.3
$x_3 x_5$	-85.9	-2.3
$x_4 x_5$	-1.6	1.9
Three-factor Interactions		
$x_1 x_2 x_3$	-127.1	-38.7
$x_1 x_2 x_4$	-57.4	27.3
$x_1 x_2 x_5$	-47.4	-7.4
$x_1 x_3 x_4$	-44.9	10.2
$x_1 x_3 x_5$	-65.4	-2.6
$x_1 x_4 x_5$	10.4	0.4
$x_2 x_3 x_4$	-22.1	-1.7
$x_2 x_3 x_5$	26.9	8.1
$x_2 x_4 x_5$	-26.4	4.8
$x_3 x_4 x_5$	-29.4	-5.8
Four-factor Interactions		
$x_1 x_2 x_3 x_4$	-14.1	7.3
$x_1 x_2 x_3 x_5$	34.4	-1.2
$x_1 x_2 x_4 x_5$	-22.4	-1.7
$x_1 x_3 x_4 x_5$	-11.9	0.7
$x_2 x_3 x_4 x_5$	-24.1	-2.7
Five-factor Interactions		
$x_1 x_2 x_3 x_4 x_5$	-34.6	-0.2
Lenth's PSE	51.6	7.2
ME	106.4	14.9
SME	202.4	28.3

Table 3. Values of the independent variables of the 2^3 factorial design of experiments and observed responses (Y_1: mass of COD removed per liter; Y_2: mass of TPh removed per liter) as well as percent removal of COD, TPh and color.

Run Order	X_1 $[COD]_0$, mg/L	X_2 Temperature, ^oC	X_5 Time, h	Y_1 COD oxidized, mg/L	Y_2 TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal
1	8100	200	1	2640	786	32	95	80
2	8100	180	1	2740	776	34	94	74
3	6300	190	1.5	1428	501	35	93	83
4	4500	180	2	1600	383	31	96	79
5	4500	200	2	1680	823	36	100	85
6	6300	190	1.5	1464	533	36	98	85
7	8100	200	2	2860	796	35	96	88
8	8100	180	2	3320	783	41	95	86
9	6300	190	1.5	1488	433	36	97	81
10	4500	200	1	1630	808	35	97	89
11	4500	180	1	1340	381	31	96	78

Table 4. Average and main effects of the independent variables and their two and higher order interactions of the 2^3 factorial design on the response factors Y_1 and Y_2.

	COD removal (Y_1)		TPh removal (Y_2)	
	Effect	*p-value*	*Effect*	*p-value*
Average Effect	2119.1	0.003	636.6	0.001
Main Effects				
X_1	1607.5	0.061	186.5	0.235
X_2	232.5	0.699	222.5	0.175
X_5	247.5	0.682	8.5	0.95
Two-factor Interactions				
$X_1 X_2$	47.5	0.936	-211	0.192
$X_1 X_5$	92.5	0.876	-0	1
$X_2 X_5$	-172.5	0.773	4	0.977
Three-factor Interactions				
$X_1 X_2 X_5$	-67.5	0.91	-2.5	0.985
SE	273.4		63	

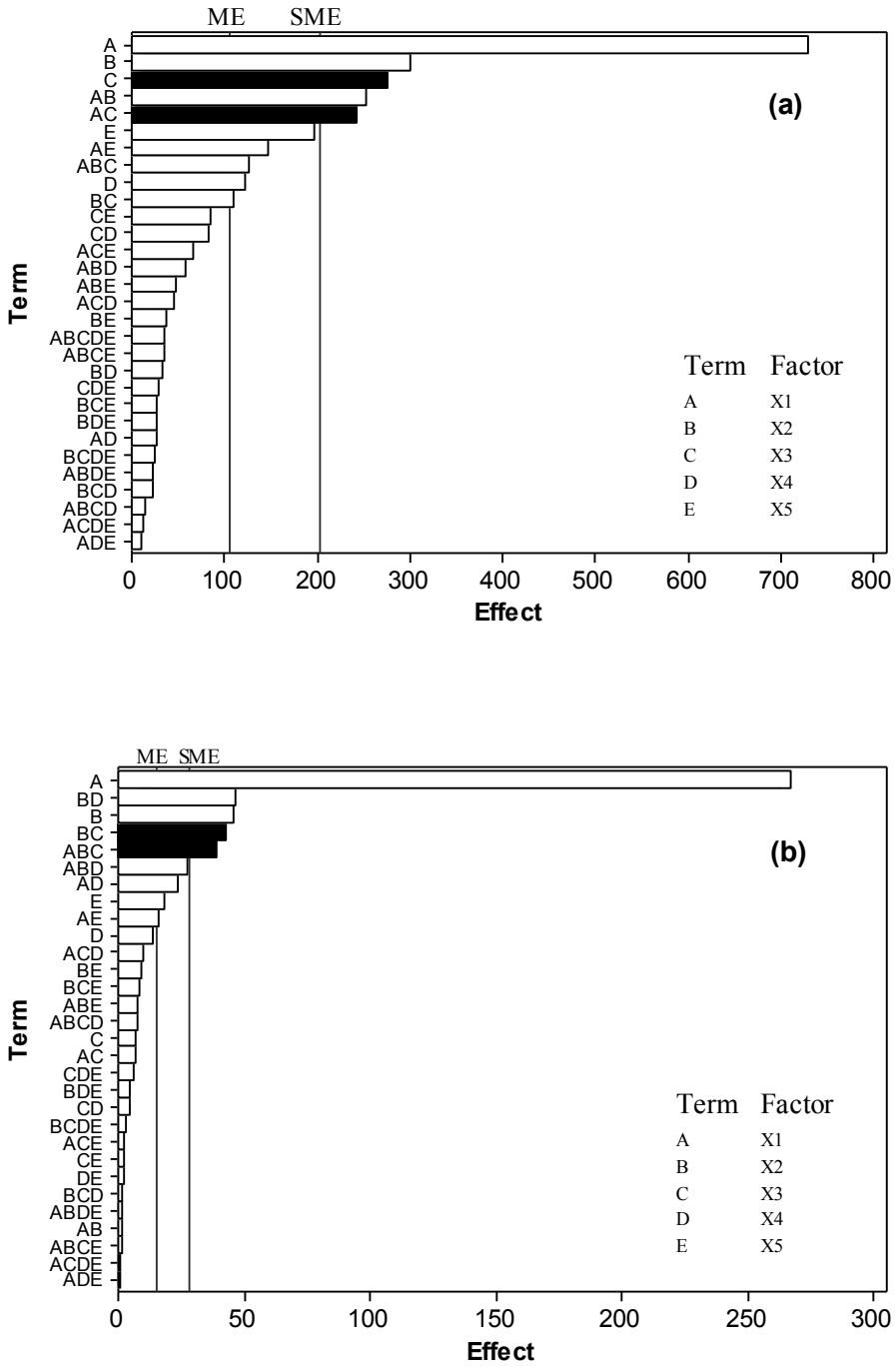

Figure 1. Pareto chart of the effects for (a) COD and (b) TPh removal for the full 2^5 factorial design of experiments. White bars: positive effects; Black bars: negative effects.

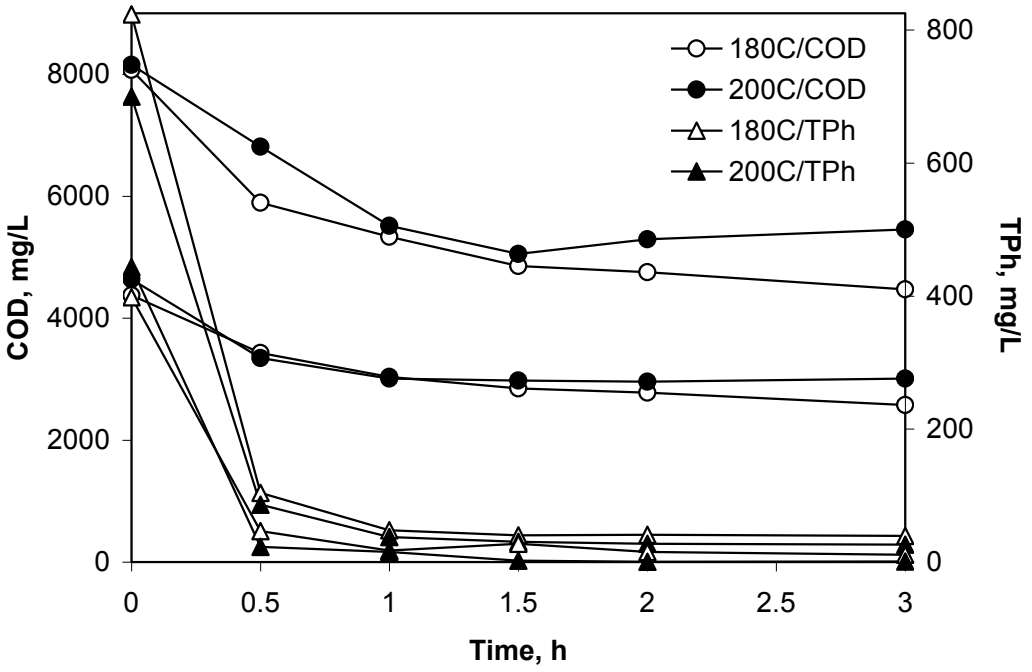

Figure 2. Evolution of COD and TPh during WAO of OMW with influent COD of 4500 mg/L or 8100 mg/L at 180°C (open symbols) and 200°C (closed symbols).